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Hot Flue Gas Spiking and Recovery Study for Tetrachlorodibenzodioxins (TCDD) Using a Modified Method 5 and SASS (Source Assessment Sampling System) Sampling with a Simulated Incinerator

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HOT FLUE GAS SPIKING AND RECOVERY STUDY FOR TETRACHLORODIBENZODIOXINS (TCDD) USING MODIFIED METHOD 5 AND SASS SAMPLING WITH A SIMULATED INCINERATOR

by

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16. ABSTRACT

The report gives results of an evaluation of the sampling and analysis of ultratrace levels of dibenzodioxins using EPA's recommended source sampling procedures (Modified Method 5 (MM5) train and the Source Assessment Sampling System --SASS). A gas-fired combustion system was used to simulate incineration flue gas, and a precision liquid injection system was designed for the program. The precision liquid injector was used to administer dilute solutions of 1,2,3,4-tetrachlorodibenzo-p-dioxin (1,2,3,4-TCDD) directly into a hot--260°C (500°F)--flue gas stream. Injections occurred continuously during the sampling episode so that very low gas-phase concentrations of 1,2,3,4-TCDD were continuously mixed with the flue gases. Recoveries were measured for eight burn experiments. For all but one, the recoveries could be considered quantitative, demonstrating efficienct collection by the EPA sampling systems. In one study, the components and connecting lines from a sampling device were analyzed separately to show where the 1,2,3,4-TCDD deposited in the train.

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ABSTRACT

This study was initiated to evaluate the sampling and analysis of ultratrace levels of chlorine substituted dibenzodioxins using U.S. Environmental Protection Agency source sampling procedures, Modified Method 5 train (MM5) and the Source Assessment Sampling System (SASS). A gas-fired combustion system was used to simulate incineration flue gas and a precision liquid injection system was designed for this program. The precision liquid injector was used to administer dilute solutions of 1,2,3,4-tetrachlorodibenzo-p-dioxin (1,2,3,4-TCDD) directly into the hot 260°C (500°F) flue gas stream. Injections occurred continuously during a sampling episode such that very low gas-phase concentrations of 1,2,3,4-TCDD were continuously mixed with flue gases.

Recoveries were measured for eight burn experiments. In all but one case, the recoveries could be considered quantitative, demonstrating efficient collection by the EPA sampling systems. In one study, the several components and connecting lines from a sampling device were analyzed separately to show where the 1,2,3,4-TCDD deposited in the train.

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SECTION 1

INTRODUCTION

This study was planned to meet the need to demonstrate reliability of sampling and analysis procedures for measuring trace levels of tetrachlorodibenzo-p-dioxin (TCDD) from an operating combustion system. The system tested was designed to reproduce the combustion gases and temperatures found while sampling hazardous waste incinerators. The series of experiments performed in this study demonstrated the ability to generate a continuous, dynamic calibration spike directly in the emission of an operating combustion system, the ability to sample the discharge with EPA source sampling techniques, and demonstrated quantitative recovery of the spike materials.

It is critical in measuring trace quantitites of organic species in combustion gas streams to use well documented procedures that have been evaluated for specific applicability to the source studied. Since the analytical process must begin with sampling, defensibility of any combustion stream study requires appropriate quality control checks at every stage in sample taking and sample handling.

In this study two sampling systems were chosen for evaluation, the Source Assessment Sampling System (SASS) train and the Modified Method 5 (MM5) train. These two EPA sampling systems have been used in sampling many source types (1-2).

Richard and Junk (3) described a dynamic injection system for spiking an incineration flue stream with a polychlorinated biphenyl standard. Recently, Petersen, et al. (4) described an experiment to spike a hot diesel engine exhaust with perdeuterated polynuclear aromatic hydrocarbon (PAH) standards to determine if a significant loss of PAH occurred during sampling and analysis.

In this study, low levels of 1,2,3,4-TCDD were continuously administered into the hot flue gas stream over a large range of concentrations which simulated the discharges reported in the literature on incineration. Overall recovery of 1,2,3,4-TCDD was used to assess the efficiency of two EPA source sampling systems to collect, retain, and stabilize ultratrace TCDD levels for subsequent analysis.

SECTION 2

RECOMMENDATIONS

The reason for performing this study was the need to evaluate EPA source sampling systems for use in hazardous waste incinerators. This is a very special combustion matrix. High temperatures and very corrosive environments are often encountered, while trace analyses are needed to demonstrate destruction removal efficiency (DRE). The laboratory techniques used in this program have demonstrated the value of the SASS and MM5 sampling systems to accurately collect low, gas-phase concentrations of TCDDs in hot flue gas. To further evaluate the performance of the sampling methods, modifications could be made to the combustion test equipment to create an environment similar to that encountered in the field during incinerator sampling. In addition to the polychlorinated dioxins and furans, several of the candidate principal organic hazardous constituents (POHCs), important as regulated species in incinerators, could also be tested.

The experiments performed in this study demonstrated the value of the gas-stream spiking system. This device could be used to perform method evaluation studies on other sampling trains as well as testing additional combustion gas matrices. The Volatile Organics Sampling Train (5) and the Dilution Tunnel sampling system (which simulates atmospheric transformations) could both be challenged by the flue gas spiking system.

The addition of reactive species found in gaseous source emissions can be administered to a slip stream of combustion gas with the dynamic spiking system. HCl and NO_2 are candidates for spiking into combustion discharges to test their reactivity under conditions found during sampling and analysis.

SECTION 3

EXPERIMENTAL PROCEDURES

EXPERIMENTAL PLAN

To test the collection efficiency of the recommended EPA sampling trains for TCDD isomers, a stack sampling program was performed. A simulated incinerator flue gas was generated using a laboratory scale furnace (see Figure 1). The flue gases from this furnace were spiked with a small quantity of 1,2,3,4-TCDD and then sampled to determine collection efficiency of the TCDD sampling system. Sampling rates and conditions were maintained at levels typical of those used with the MM5 or SASS sampling trains.

TEST STRATEGY

A pilot plant furnace was used to generate the simulated incinerator flue gas. A low flow rate pump was used to inject a TCDD sample solution into this flue stream at a point where the gas temperature was approximately 260°C (500°F). Flue gases were then sampled by the stack sampling equipment. The oxygen content of the flue gas stream was approximately 10-12% O_2 (85% excess air) in all tests. The sampling temperatures, rates, and volumes were typical of those used in a MM5 or SASS apparatus. Since TCDDs are highly toxic compounds, it was imperative that none of the sample escaped. To prevent such losses, all gases spiked with 1,2,3,4-TCDD were passed through the sampling train, and a charcoal trap was used as a secondary collector. A schematic diagram (Figure 2) shows the experimental arrangement: natural gas combustor outlet; hot gas spike injection; sampling train; charcoal safety trap; and gas moving system.

COMBUSTION AND SAMPLING SYSTEMS

The SASS apparatus is capable of sampling particualte and vapor emissions from stationary sources (6). The EPA Method 5 technique is normally used only in particulate sampling of stationary sources, but with the addition of a resin sorption bed it can be used to assess condensible organic emissions as well.

In this program, the SASS equipment was operated in accordance with procedures outlined in the EPA Level 1 manual (6). Because a relatively clean fuel (natural gas) was used to produce the flue gas stream sampled,

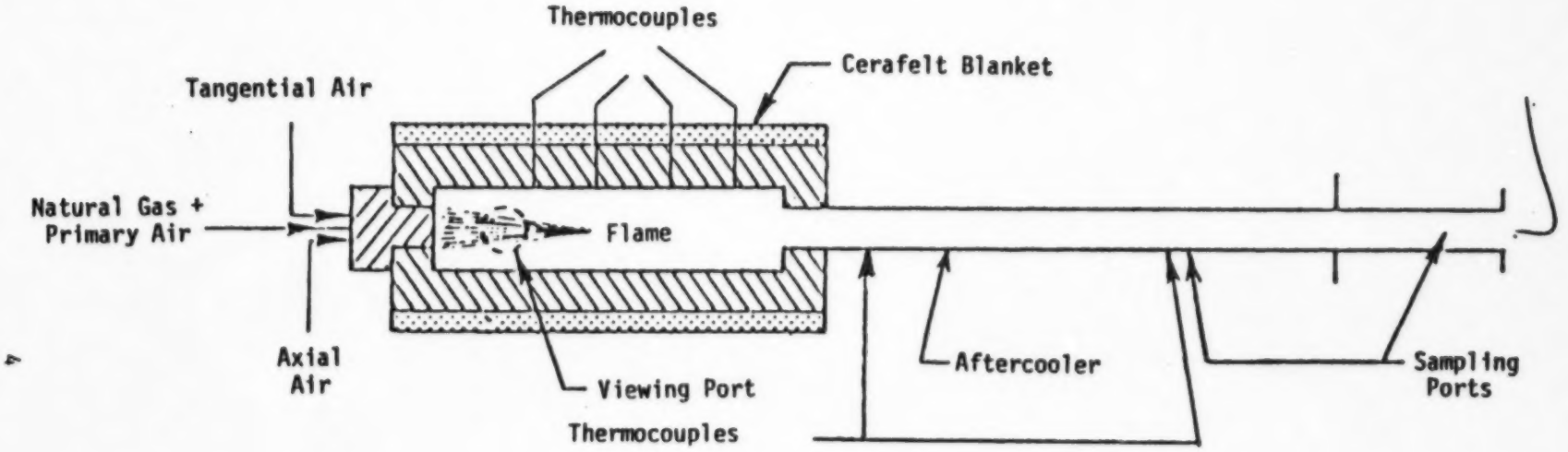

Figure 1. Natural gas combustor

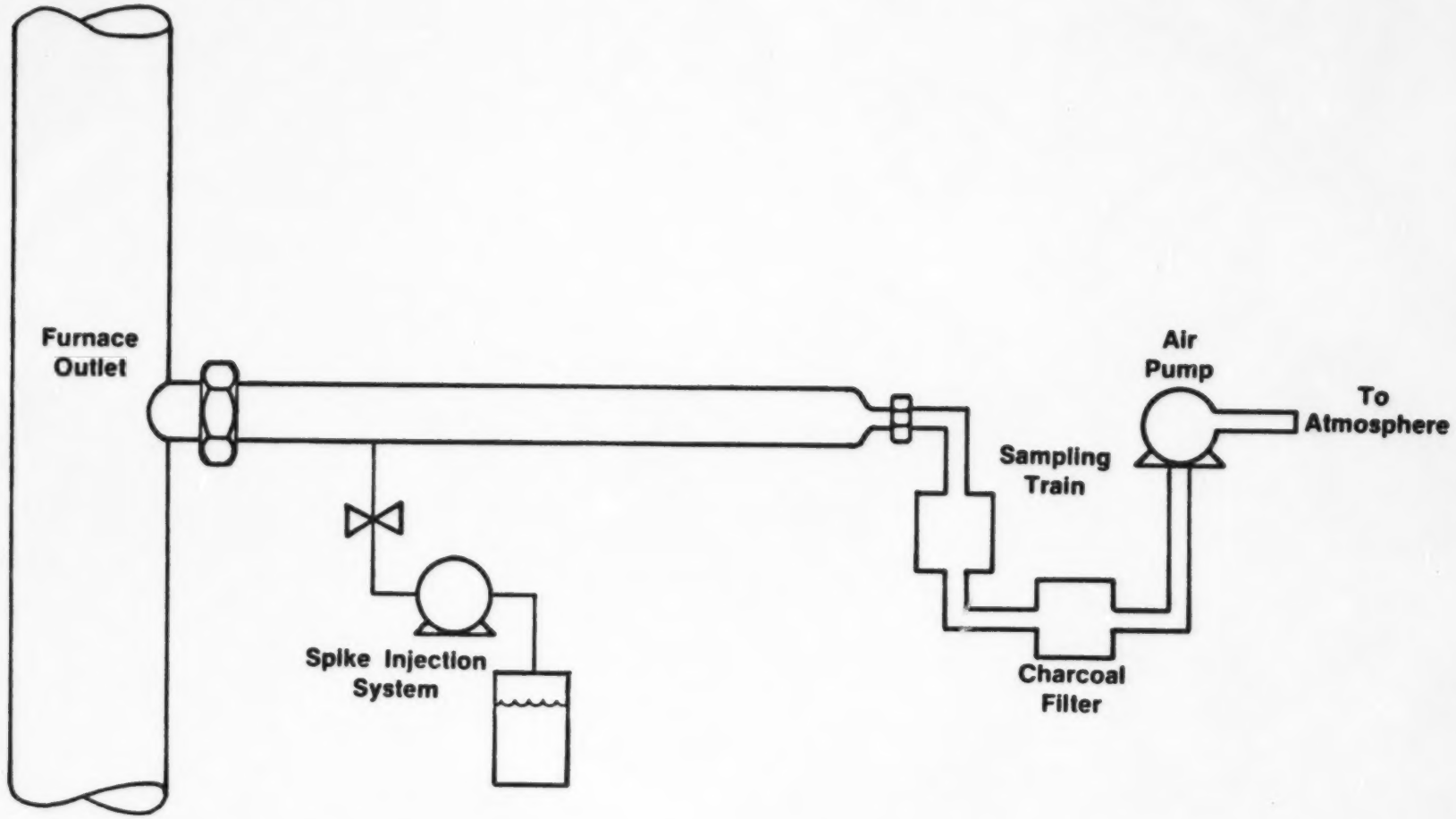

Figure 2. TCDD injection and sampling apparatus

some modifications were made to the standard SASS apparatus. The normal stack sampling probe and cyclones were replaced with borosilicate glass connecting tubing. The stainless steel cyclones were removed to simplify equipment turnaround. The solutions that would normally be contained in impingers 1 and 2 were eliminated, but the impingers were left in the system as condensate traps. Impinger 3 contained a charge of activated charcoal to serve as a backup trap in the event that 1,2,3,4-TCDD escaped collection in the resin bed. Impinger 4 contained a charge of silica gel to protect the sampling pumps and dry gas meter. The modified SASS sampling apparatus is shown in Figure 3.

The major difference between the SASS and MM5 trains is in the sampling rate and volume of gas collected. This gas volume allows the use of a smaller quantity of XAD-2 in the MM5 train. The filter is typically held at a higher temperature in the SASS train. The MM5 train and location of gas-phase spiking are shown in Figure 4.

A development of this study was a gas-phase spiking system that could simulate the presence of trace quantities of pollutants such as certain TCDD isomers in hot flue gas streams. A spiking system was designed that could administer liquid solutions of the spike material, in this case, the 1,2,3,4-tetrachlorodibenzo-p-dioxin into the gas stream. The spiking apparatus is illustrated in Figure 5. A quartz capillary line was used to transfer the dioxin solution from a precision metering pump to the flue gas stream. Condensation was prevented by jacketing the capillary at the point where heating occurred. By circulating a refrigerant around the transfer line up to the point where the capillary discharged into the hot flue gas, premature vaporization and condensation were prevented. The primary solvent was acetone and a keeper, 0.05% (v/v) decane, was added to the dioxin-acetone solution in order to wet the final segment of transfer line and prevent deposition of the small amount of 1,2,3,4-TCDD in the capillary tip.

As shown in Figure 5, a slip stream was drawn from the primary combustion discharge. The transfer line in which solution spiking occurred was insulated and externally heated to maintain the required gas stream temperatures from the point of spiking into the samplers (SASS and MM5). The combustion gases were generated in a small, ceramic-lined tube furnace fired with natural gas. The furnace was nominally operated at 100 MJ/hr at approximately 5% O_2 (dry). A slip stream of flue gas was diverted from the furnace exhaust into the sampling apparatus. A summary of operational parameters for the flue gas sampling systems is shown in Table 1. For both the SASS and MM5 tests, the flue gas temperature at the injection point was 260°C (500°F). The filter temperature in the SASS is typically held at 204°C (400°F), whereas the Method 5 procedures (40 CFR 60, Appendix A) specify a 120°C (250°F) filter temperature. The operating upper temperature limit for the XAD-2 traps was set at 20°C (68°F). Water at ice temperatures was circulated in the jacketed condensers shown for both the SASS and MM5 trains. As illustrated in Figure 3, a double condenser section was necessary to achieve 20°C in the SASS train.

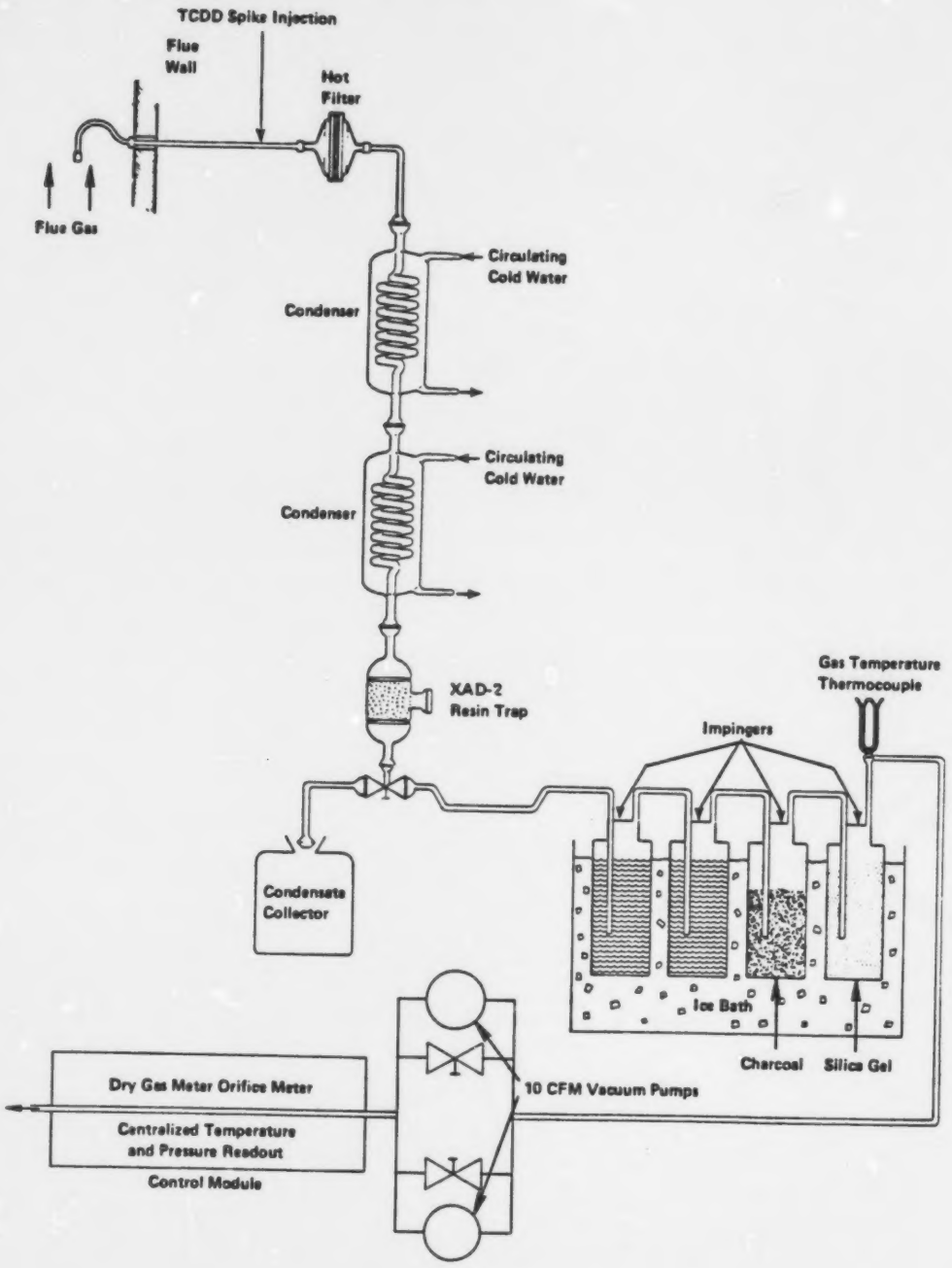

FIGURE 3. MODIFIED SOURCE ASSESSMENT SAMPLING SYSTEM (SASS)

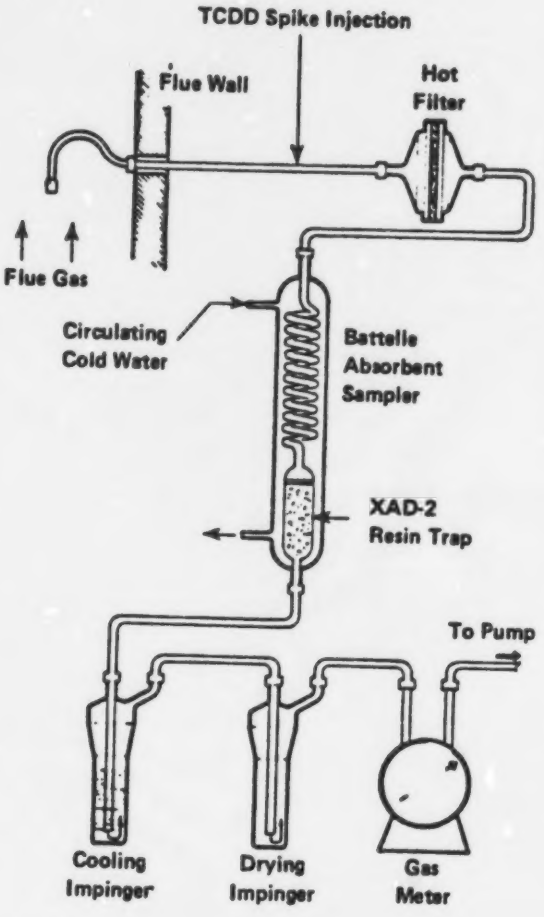

FIGURE 4. MODIFIED METHOD 5 SAMPLING SYSTEM (MM5).

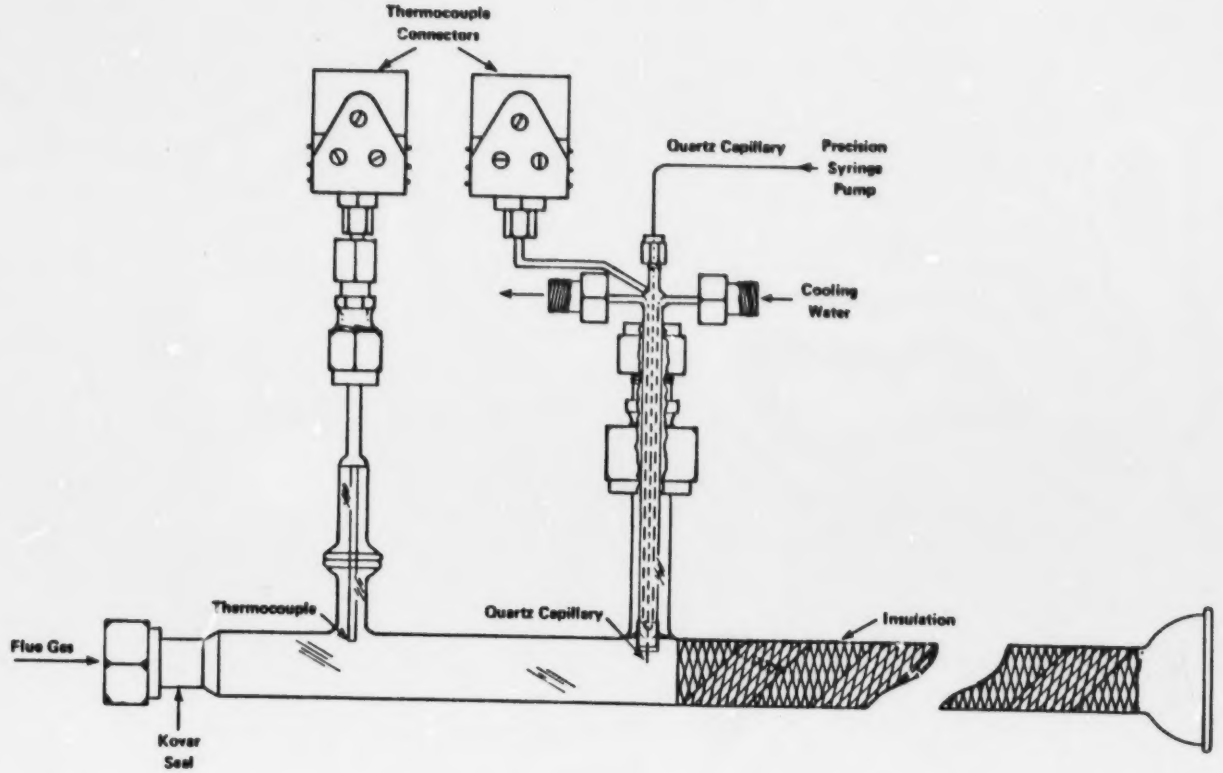

Figure 5. Battelle gas stream injection system

TABLE 1. OPERATING PARAMETERS FOR THE SAMPLING SYSTEMS

Fuel	Natural Gas
Sampling Volumes	
SASS	30 m^3 (1060 ft^3)
MM5	6.0 m^3 (200 ft^3)
Flue Gas Sampling Rate	
SASS	0.11 m^3/min (4 scfm)
MM5	0.02 m^3/min (0.8 scfm)
Spike Solution Injection Rate	Approximately 0.2 mL/min
Filter Temperatures	
SASS	204°C (400°F)
MM5	120°C (250°F)
XAD-2 Resin Bed Temperatures	
SASS	20°C (68°F)
MM5	20°C (68°F)

Level 1 aguidelines set total dry gas volumes sampled by the SASS at 30 m^3. For the Method 5 train sampling volumes are source specific. Relatively large sample volumes were taken for MM5 tests to insure collection times similar to actual field operation of the sampling system in incinerator applications. A total of 10 tests (numbered 1 through 10) were conducted during this program. The experimental outline is shown in Table 2. The tests were divided into two series: 1-6 and 7-10. The first series consisted solely of SASS equipment and Level 1 operational procedures while the second series employed MM5 equipment. The first test (Test 1) was a blank run to identify native concentrations of 1,2,3,4-TCDD and 2,3,7,8-TCDD produced either by the furnace or by sample handling. Test 2 was a room air test in which a known quantity of 1,2,3,4-TCDD was injected into the sample train; however, a dry heated air stream was used as the sampled gas. Tests 3-6 employed the SASS sampling train with simulated incineration discharge gas and variable spike levels of 1,2,3,4-TCDD.

The MM5 tests (7-10) were completed in a similar manner using hot combustion gas starting with the highest 1,2,3,4-TCDD concentration and progressing to the lowest concentration. Tests 9 and 10 were run at the same concentrations to determine experimental reproducibility.

The TCDD concentrations shown in Table 2 were the intended concentrations. Actual concentrations varied somewhat for each test. Prior to beginning each experiment, all glassware was thoroughly cleaned with methylene chloride and baked in a clean oven at 400°C (752°F) for 16 hours. The sampling equipment was then assembled in the combustion engineering laboratory and attached to the tube furnace. The sampling systems were leak checked prior to commencing an experiment. Leak rates for the SASS train were typically 8.5×10^{-4} m^3/min at 635 torr. Leak rates for the MM5 equipment were typically 3.1×10^{-4} m^3/min at 635 torr. To begin the experiment, the gas sampling pumps were started and temperatures allowed to equilibrate. After sampling rates were set and operating temperatures reached the precision metering pump was turned on and set at an injection rate of 0.17-0.18 mL/min. Table 3 gives a summary of actual system conditions during each combustion test.

TABLE 2. EXPERIMENTAL OUTLINE

Test Number	Gas	Sample[a] Concentration	Sampling Apparatus	Sample
1	Flue Gas	0	SASS	Blank
2	Hot Air	1000	SASS	1,2,3,4-TCDD
3	Flue Gas	1000	SASS	1,2,3,4-TCDD
4	Flue Gas	1000	SASS	1,2,3,4-TCDD
5	Flue Gas	100	SASS	1,2,3,4-TCDD
6	Flue Gas	10	SASS	1,2,3,4-TCDD
7	Flue Gas	1000	MM5	1,2,3,4-TCDD
8	Flue Gas	100	MM5	1,2,3,4-TCDD
9	Flue Gas	10	MM5	1,2,3,4-TCDD
10	Flue Gas	10	MM5	1,2,3,4-TCDD

(a) Flue gas concentration (pg/m^3) at 20°C.

CHEMICAL ANALYSES

The solvents used, hexane, benzene, carbon tetrachloride, and methylene chloride, were Distilled-in-Glass grade (Burdick and Jackson Laboratories, Inc., Muskegon, MI). Alumina and silica gel were purchased from BioRad

TABLE 3. SYSTEM OPERATING CONDITIONS

Test Number	1	2	3	4	5	6	7	8	9	10
Gas Temperature, °C[(a)]	260	233	263	254	257	251	258	258	256	262
Filter Temperature, °C	203	212	201	193	187	208	130	128	129	129
XAD-2 Temperature, °C[(b)]	5.0	5.0	6.1	6.67	8.44	7.22	6.67	6.28	5.44	6.11
O_2, Percent	5.0	5.0	5.1	4.9	4.7	4.9	4.7	5.0	5.1	4.9
Carbon Dioxide, % (v/v)	0	9.6	9.0	9.2	9.1	9.2	9.4	9.4	9.2	9.3
Carbon Monoxide, ppm (v/v)	0	<25	<25	<25	<25	<25	<25	<25	<25	<25
Sampling Rate, m^3/min	0.113	0.112	0.112	0.114	0.116	0.117	0.021	0.021	0.021	0.021
Gas Volume Sampled, m^3 (c)	28.7	30.2	30.6	30.2	30.7	30.7	5.50	5.54	5.69	5.53
Solvent Injection Rate, mL/min	0.18	0.17	0.17	0.17	0.17	0.18	0.17	0.17	0.18	0.17

(a) Gas temperatures measured at the point of injection.
(b) Temperatures measured at XAD-2 outlet.
(c) Dry volumes at 20°C.

Laboratories, Richmond, CA. These were solvent rinsed and activated immediately prior to being used. The 2,3,7,8-tetrachlorodibenzo-p-dioxin-$^{13}C_{12}$ (2,3,7,8-TCDD-$^{13}C_{12}$) was purchased from KOR Isotopes, Cambridge, MA, and the 1,2,3,4-tetrachlorodibenzo-p-dioxin (1,2,3,4-TCDD) was purchased from Ultra Scientific, Inc., Hope, RI. All analytical glassware was washed with soap and water, rinsed with reagent grade acetone, and baked at 450°C for a minimum of 12 hours prior to use. The XAD-2 resin, precleaned grade (Supelco, Inc., Bellefonte, PA) was extracted for 24 hours with methylene chloride prior to being packed into the sampling modules. Test batches of resin were extracted and blanks checked by glass capillary GC-FID prior to use.

Sample Extraction and Cleanup

The XAD-2 resin samples were Soxhlet extracted for 16 hours with methylene chloride. The 125 g resin samples from the SASS experiments were spiked with 2 ng of internal standard (2,3,7,8-TCDD-$^{13}C_{12}$) prior to extraction, while the 22 g XAD-2 resin samples from the MM5 experiments were spiked with 800 pg of 2,3,7,8-TCDD-$^{13}C_{12}$. The extraction volumes were one liter for the SASS samples and 200 mL for the MM5 samples.

The methylene chloride extracts were concentrated to approximately 10 mL using a Kuderna-Danish concentrator. The concentrated extracts were transferred to concentrating tubes (with drawn out tips) using three 2 mL hexane rinses and carefully taken to near dryness using a gentle stream of dry nitrogen. The extracts were then redissolved in 5 mL of hexane.

The extracts were cleaned using a series of column chromatography steps: silica, modified silica, and alumina. The extracts were first passed through a multilayered silica column containing silica, 44% sulfuric acid on silica, and 33% sodium hydroxide (1 M) on silica, in layers. The column was prerinsed with 20 mL hexane and extract was added, followed by column elution with 10 mL 1:1 hexane/benzene. The total eluent was collected and concentrated to about 1 mL using a gentle stream of dry nitrogen. The extract was redissolved in 5 mL of hexane and added to a column containing 5 g of precleaned and activated alumina. This column was sequentially eluted with 15 mL hexane, 25 mL hexane/carbon tetrachloride (1:1), and 20 mL hexane/methylene chloride (1:1). The hexane/methylene chloride fraction was collected and gently taken to near dryness. The extract was dissolved in 20 L of n-decane and stored at 0°C until analyzed. The column chromatography clean-up procedure is shown in Figure 6.

HRGC/HRMS Procedure

The extracts were analyzed by combined high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). A VG Model 7070H HRMS directly coupled to a Carlo Erba Model 4160 GC was used for analyses. Data was acquired by a VG Model 2035 foreground/background data system. The MS was operated in the electron impact ionization mode at a mass resolution of 10,000-12,000 (M/ M, 10% valley).

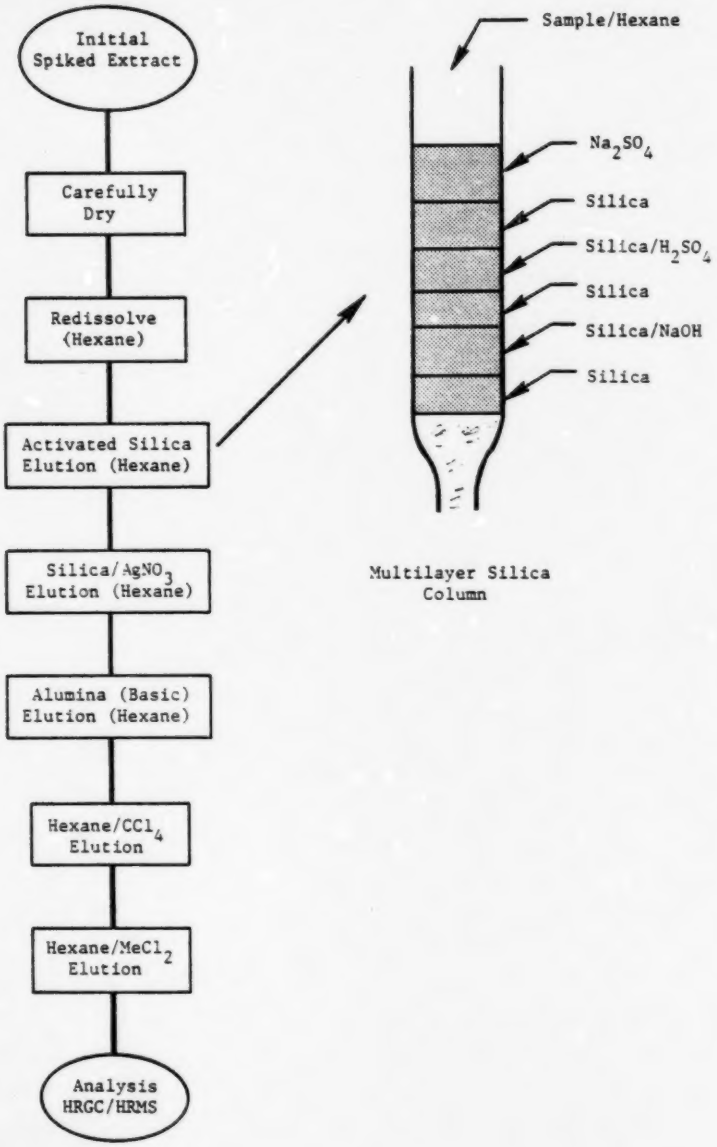

Figure 6. Schematic diagram of the sequential TCDD cleanup procedure.

Five ion masses were monitored using the VG Digital Multiple Detection (MID) unit which included a prototype 20-bit digital-to-analog converter for accelerating voltage and electrostatic analyzer voltage control. The monitored masses were: 319.8965 and 321.8936, the most intense peaks in the molecular ion cluster of native TCDDs along with 331.9368 and 333.9338 the most intense peaks in the molecular ion cluster of the internal standard; and 318.9792, a peak for perfluorokerosene used as a check mass by the data system to maintain mass focus.

The chromatographic column was a 30 m, DB-5 coated fused silica capillary interfaced directly into the ion source. Helium carrier was used at a flow velocity of 21 cm/sec. Sample injection was made at 150°C with a 3 min hold time followed by a linear temperature increase of 30°C/min to 280°C. The final temperature was maintained for 12 min. Under these conditions, 2,3,7,8-TCDD-$^{13}C_{12}$ and 1,2,3,4-TCDD had retention times of approximately 13 min each.

Sample Workup and Quality Assurance

Tests 1 and 2 were baseline tests. Test 1 was a system blank in which native TCDDs from the sampling system and analytical procedures were tested. Test 2 was a room air test using the SASS sampler at the highest spike concentration. A test protocol was established for Tests 1 (system blank) and 2 (dry gas spiking) which allowed individual analysis of each part of the SASS sampling train. A 70 to 130% total recovery of spiked 1,2,3,4-TCDD was established as a criterion for proceeding from Test 2 through the series of experiments in Tests 3-10.

SECTION 4

RESULTS AND DISCUSSION

The analytical determinations on Test 1 (system blank using flue gas) and Test 2 (system spike using heated air) were completed before the actual SASS/MM5 challenge tests were performed. No detectable 1,2,3,4-TCDD or 2,3,7,8-TCDD was found at the minimum detectable amount (1 pg injected) for Test 1. For Test 2, subsamples were analyzed representing several regions of the SASS train, regions where TCDDs might condense or accumulate. The results of those analyses are shown in Table 4 where recoveries are shown to total ~92%. An instrument fault occurred in the computer system while computing the XAD-2 extract data and the reported 70% recovery could not be verified by exact area computation. This value is approximate but represented the major portion of the 1,2,3,4-TCDD and showed a high recovery overall for the system spike.

TABLE 4. EPA INCINERATION SIMULATION RECOVERIES-TEST 1

Spike Level Internal Standard	Amount of 1,2,3,4-TCDD	Percent Recovery	SASS Test Section
2000 pg	50 pg	0.2	Injector liner
2000 pg	ND(a)	--	Heated flue
2000 pg	260 pg	1.1	Filter
2000 pg	4800 pg	21	Transfer line to XAD-2
2000 pg	17500 pg	70(b)	XAD-2 resin
		Total recovery ~92%	

(a) Not detected.
(b) Approximate.

CHOICE OF SPIKE LEVELS FOR TESTS 2-10

Some reported TCDD levels are shown in Table 5. These data have received much attention and to date no definitive study of incinerator discharge levels for TCDDs has been performed. The proposed analytical system is capable of sub-picogram sensitivity for individual TCDD isomers and spiking levels of 1000, 100, and 10 pg/m^3 were proposed. Based on typical collection volumes for the SASS and Modified Method 5 trains, the total weight of 1,2,3,4-TCDD spike ranged from 60 pg to 30 ng as shown in Table 6. A syringe volume of 50 mL was used in the precision metering pump to deliver the dioxin spike solution; and since gas collection rates of 6.8 m^3/hr for the SASS train and 1.3 m^3/hr for the MM5 train were used in sample collection, 1,2,3,4-TCDD spike solutions of 1-600 ng/L concentration were required (Table 7). This corresponds to an approximate delivery rate of 0.17-0.18 mL/min. This rate was high enough to flush the transfer probe and prevent condensation in the capillary.

The choice of an optimum solvent was based on delivery rate, viscosity, solubility of 1,2,3,4-TCDD, boiling point, XAD-2 retention, and demonstrated purity. The solvent system used was acetone with 5% (v/v) decane as a "keeper". Decane acted to flush residual TCDD from the transfer probe. The acetone acted as a volatile carrier for the 1,2,3,4-TCDD and was discharged from the XAD-2 resin bed and did not interfere with TCDD collection.

TABLE 5. SOURCE LEVELS OF TCDD (7)

Source	Level
Rotary Kiln, Supplementary Fuel	None
Rotary Kiln, No Supplementary Fuel	110-8200 ppb (2,3,7,8)
Rotary Kiln Water Wash Particulates	2500 ppb (All isomers)
Residential Combustion Source	0.6 ppb (2,3,7,8)

TABLE 6. TOTAL TCDD SPIKED

Spike Level	Spike Concentration	Total TCDD SASS (30 m^3)	Total TCDD MM5 (6 m^3)
High	1000 pg/m^3	30 ng	6.0 ng
Medium	100 pg/m^3	3 ng	0.6 ng
Low	10 pg/m^3	300 pg	0.06 ng

TABLE 7. SOLUTION CONCENTRATIONS FOR SPIKING

Spike Level	Solution Concentration (S SS)	Solution Concentration (MM5)
High	600 ng/L	120 ng/L
Medium	60 ng/L	12 ng/L
Low	6 ng/L	1.2 ng/L

RECOVERY STUDIES--TESTS 3-10

Tests 3-10 were designed to challenge both the SASS and MM5 sampling systems at gas-phase concentrations that were expected to cover a range from high levels to the minimum levels detectable by available analytical methodology. Results of this series of experiments are given in Table 8 which includes the dry air spike experiment (Test 2).

These data show good internal consistency and high recoveries for each experiment, except Test 10, where a 229% recovery was observed. No experimental explanation exists for this unusual result. On balance the data show that both the SASS and MM5 trains work well with the isotope standard, HRGC/HRMS analytical technique, to measure TCDDs (modeled by recovery of 1,2,3,4-TCDD) from hot flue gas streams.

It is interesting to note in Test 2, the dry air experiment, that a major portion of the spiked 1,2,3,4-TCDD was found in the filter (~1%) and cold regions of transfer tubing leading into the resin trap (~23% in transfer line). To investigate the effect of moisture condensation on operation of the sampling systems in flue gas, two separate investigations were performed. For the SASS samples (Tests 3-6) the heated "front half" of the train (probe rinse, filter housing, filter, and heated transfer line wash) was analyzed separately from the cooled "back half" of the train (cooled transfer line washes, resin bed, and condensate). In all four experiments, less than 1% of the spiked 1,2,3,4-TCDD was found in the "front half" of the SASS train. A second series of experiments were performed to determine the possibility of TCDD breakthrough from the resin trap. For this purpose, the condensates from Tests 3-6, the SASS challenge tests, were analyzed separately to determine if any of the spiked 1,2,3,4-TCDD was carried through the resin bed with condensed water. After extraction and concentration, no measurable levels of 1,2,3,4-TCDD could be detected in the condensates from Tests 3-6, demonstrating the effectiveness of XAD-2 to trap TCDDs even in moisture laden combustion gas streams.

This set of ten experiments demonstrated the ability of two EPA source sampling trains to collect and stabilize TCDDs for subsequent analysis. The model compound used, 1,2,3,4-TCDD, is probably a good representative of all the tetrachlorodibenzo-p-dioxins. The other isomeric members of this class of compounds, PCDDs and PCDFs, should be equally well analyzed by the technique used in this study.

TABLE 8. 1,2,3,4-TCDD RECOVERIES FROM TESTS 2-10

Test Number	Sampling System	Liquid Spike Volume(ml)	1,2,3,4-TCDD Liquid Concentration(pg/ml)	320/322 Ratio[a]	332/334 Ratio[b]	Expected Concentration (ng)	Calculated Concentration (ng)	Percent Recovery
2 (Dry Air)	SASS	49	500	--	--	--	--	92
3	SASS	51	500	0.79	0.81	25	18	72
4	SASS	42	500	0.80	0.82	21	17	81
5	SASS	51	50	0.78	0.78	2.5	2.9	116
6	SASS	51	5	0.76	0.78	0.26	0.28	108
7	MM5	47	150	0.81	0.84	7.1	8.0	113
8	MM5	47	12	0.78	0.81	0.56	0.57	102
9	MM5	49	8	0.81	0.80	0.39	0.47	121
10	MM5	47	8	0.80	0.81	0.38	0.87	229

(a) Area ratio of principal fragment ions of 1,2,3,4-TCDD.
(b) Area ratio of principal fragment ions of 2,3,7,8-TCDD-$^{13}C_{12}$.

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(*) NTIS No. PB292931.
(**) NTIS No. PB293795.

Appendix A

TASK QUALITY ASSURANCE (QA) AUDIT

Date of Audit July 24, 1984

Task No. 131 Contract No. 68-02-2686

Task Title Hot Flue Gas Spiking and Recovery Study for Tetrachlorodibenzo-p-dioxins

Task Manager _____ Task Officer _____

Comments: An audit of the experimental record of the above task was conducted to determine completeness to the extent that the record could be studied in retrospect

Applicable Documents: Laboratory Record Books 37273, 37488, 37543

Sampling and Sample Tracking: Sampling conducted at Battelle; procedures clearly defined, sample identification fair. These records are in Record Book 37273.

Analyses--Laboratory Activities: These activities are described in Laboratory Record Books 37488 and 37534; the former describes sample preparation starting on page 45 and the latter lists samples analyzed by HRGC/HRMS. The analysis record is on a track tape and can be found from the file number listed with sample run identification, in the mass spectrometry magnetic tape storage facility

Approved by QA Officer: R.E. Hefflefinger